

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B41M 5/00, C09D 133/02, 129/04	A1	(11) International Publication Number: WO 98/55328 (43) International Publication Date: 10 December 1998 (10.12.98)
---	----	---

(21) International Application Number: PCT/US98/09882	(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 15 May 1998 (15.05.98)	Published <i>With international search report.</i>
(30) Priority Data: 08/868,415 3 June 1997 (03.06.97) US	
(71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US).	
(72) Inventors: PEKALA, Richard, W.; 3103 Henrich Farm Lane, Allison Park, PA 15101 (US). HILL, Charles, T.; 211 Lynn Drive, New Brighton, PA 15066 (US).	
(74) Agents: MORRIS, George, D.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.	

(54) Title: COATING COMPOSITION AND PRINTING MEDIUM**(57) Abstract**

A printing medium comprising (a) a substrate having at least one surface, and (b) a coating on the surface wherein the coating comprises (1) binder comprising poly[(meth)acrylic] acid and poly(vinyl alcohol), and (2) particulate hydrophilic amorphous silica dispersed in the binder, wherein at least 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.01 to 25 μm . An aqueous coating composition comprising the above binder and amorphous silica is also described.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

COATING COMPOSITION AND PRINTING MEDIUM

The present invention is in respect of printing media which may be inkjet printed, to a method of inkjet printing on the printing media, and to coating compositions which may be used to form the printing media.

Inkjet printing produces little noise and can be used to print single color images or multicolor images on various substrates. Plain paper or paper having a low degree of sizing can be used as the printing substrate, but these suffer from the disadvantage that a clear image cannot be obtained because of the diffusion of the ink into the paper. More particularly, the image lacks sharp resolution, and in the case of color printing, the image lacks good optical density.

In order to achieve inkjet printed images of improved quality, coated papers have been employed as the printing substrates. The image quality varies depending upon the type of coating employed. In most instances image quality is better than that obtained using uncoated paper, but it is still less than desired.

Similarly, inkjet printing has been used to print single color images or multicolor images on organic polymer media, but spreading of the ink on organic polymer surfaces presents many problems, including lack of sharp image resolution, and in the case of color printing, the image lacks good optical density and wide color gamut. Coatings have provided some improvement, but image quality is still far less than desired.

Adhesion of coatings to paper substrates is often not a problem. However adhesion of inkjet printable coatings to organic polymer substrates has been a problem, especially in respect of polyolefin substrates.

- 2 -

Inkjet printing inks contain large amounts of solvents which, after printing, must either be permanently retained by the printing medium or, as is most common, evaporated. In order to avoid introduction of large amounts of organic materials into the environment, aqueous solvents which contain few, if any, organic materials, are generally used. Restriction to aqueous solvents, however, has heretofore resulted in coatings having low adhesion to organic polymer substrates and providing low quality images when inkjet printed.

Coating compositions have now been found which although based on aqueous solvents, do result in coatings of improved adhesion and high quality inkjet printed images.

Accordingly, one embodiment of the invention is a coating composition comprising: (a) volatile aqueous solvent; (b) binder dissolved in the volatile aqueous solvent, the binder comprising water-soluble poly[(meth)acrylic] acid and water-soluble poly(vinyl alcohol); and (c) particulate hydrophilic amorphous silica wherein at least 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.01 to 25 μm .

Another embodiment of the invention is a printing medium comprising: (a) a substrate having at least one surface; and (b) a coating on the surface wherein the coating comprises: (1) binder comprising poly[(meth)acrylic] acid and poly(vinyl alcohol); and (2) particulate hydrophilic amorphous silica dispersed in the binder, wherein at least 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.01 to 25 μm .

Yet another embodiment of the invention is a printing process which comprises applying liquid ink droplets to the printing medium of the second embodiment.

- 3 -

It is important that the poly[(meth)acrylic] acid, the poly(vinyl alcohol), and the hydrophilic particulate silica all be concurrently present in the coating compositions and the coatings of the printing media. Although it is desired not to be bound by any theory, it is believed that many improvements resulting from the present invention are due to the large numbers of sites available for hydrogen bonding among the three essential components of the coating.

The volatile aqueous solvent is predominately water. 10 Small amounts of low boiling volatile water-miscible organic solvents may be intentionally added for particular purposes. Examples of such low boiling volatile water-miscible organic solvents include methanol [CAS 67-56-1], ethanol [CAS 64-17-5], 1-propanol, [CAS 71-23-8], 2-propanol [CAS 67-63-0], 2-butanol [CAS 78-92-2], 2-methyl-2-propanol [CAS 75-65-0], 2-propanone [CAS 67-64-1], and 2-butanone [CAS 78-93-3]. The listing of such solvents is by no means exhaustive.

It is preferred that substantially no low boiling volatile water-miscible organic materials be intentionally added to the system in order to minimize organic solvent emissions upon drying the coating.

Similarly, water-miscible organic solvents which are of low, moderate, or even negligible volatility may be 25 intentionally added for particular purposes, such as for example, retardation of evaporation. Examples of such organic solvents include 2-methyl-1-propanol [CAS 78-83-1], 1-butanol [CAS 71-36-3], 1,2-ethanediol [CAS 107-21-1], and 1,2,3-propanetriol [CAS 56-81-5]. The listing of such 30 solvents is by no means exhaustive.

It is preferred that substantially no water-miscible organic solvents which are of low, moderate, or negligible volatility be intentionally added to the system.

- 4 -

Notwithstanding the above, those materials which, although not intentionally added for any particular purpose, are normally present as impurities in one or more the components of the coating compositions of the invention and 5 which become components of the solvent, may be present at low concentrations.

In most instances water constitutes at least 80 percent by weight of the volatile aqueous solvent. Often water constitutes at least 95 percent by weight of the 10 volatile aqueous solvent. Preferably water constitutes substantially all of the volatile aqueous solvent.

The water-soluble poly[(meth)acrylic acid] is water-soluble addition polymer formed by polymerizing monomer comprising acrylic acid [CAS 79-10-7], methacrylic acid 15 [CAS 79-41-4], or both acrylic acid and methacrylic acid. Water-soluble poly[(meth)acrylic acid] and its preparation are both well known. See Encyclopedia of Polymer Science and Technology, vol. 1, John Wiley & Sons, New York (1964), Library of Congress Catalog Card Number 64-22188, pages 197-226, the disclosure of which is incorporated herein by reference. Acrylic and methacrylic acids are readily copolymerized with many other monomers. The poly[(meth)acrylic acid] may contain mer units of such other monomers unless their numbers or identities cause the 25 poly[(meth)acrylic acid] to be water-insoluble. Examples of monomers which may be copolymerized with acrylic acid and/or methacrylic acid include methyl acrylate, methyl methacrylate, 2-hydroxyethyl acrylate, styrene, and vinyl acetate. In most cases the poly[(meth)acrylic acid] is a homopolymer of acrylic acid, a homopolymer of methacrylic acid, or a copolymer of 30 acrylic acid and methacrylic acid.

- 5 -

The weight average molecular weight of the water-soluble poly[(meth)acrylic acid] may vary widely. In general, the weight average molecular weight should be at least as large as will permit the poly[(meth)acrylic acid] to form films, but not so large as will render the binder insoluble in the volatile aqueous solvent. Usually the weight average molecular weight of the poly[(meth)acrylic acid] is in the range of from 100,000 to 1,000,000. Often the weight average molecular weight is in the range of from 150,000 to 500,000.

From 200,000 to 300,000 is preferred.

The water-soluble poly(vinyl alcohol) and its preparation are both well known. See Encyclopedia of Polymer Science and Technology, vol. 14, John Wiley & Sons, New York (1971), Library of Congress Catalog Card Number 64-22188, pages 149-207, the disclosure of which is incorporated herein by reference. Water-soluble poly(vinyl alcohol) is usually made either by (1) direct hydrolysis of a poly(vinyl ester) or (2) ester interchange with an alcohol such as methanol or ethanol. Other processes are known, but little used. All of these processes will hereinafter be referred to collectively as "hydrolysis". By far the most common poly(vinyl ester) used in these processes is poly(vinyl acetate). In most cases the poly(vinyl acetate) is a homopolymer, so that the poly(vinyl alcohol) is a homopolymer if hydrolysis is complete, or a copolymer of vinyl alcohol and vinyl acetate if hydrolysis is less than complete. Since vinyl acetate can be copolymerized with many other monomers, vinyl alcohol copolymers are readily available by the hydrolysis of the vinyl acetate copolymers. Irrespective of whether other monomers are copolymerized with the vinyl acetate (or other vinyl ester), the numbers of hydroxyl groups present in the resulting poly(vinyl alcohol) are sufficient to render the poly(vinyl alcohol) water-soluble. In most instances the

- 6 -

water-soluble poly(vinyl alcohol) is characterized by a degree of hydrolysis of at least 75 percent. Often the water-soluble poly(vinyl alcohol) is characterized by a degree of hydrolysis of at least 80 percent. Preferably the degree of hydrolysis 5 is at least 85 percent. As used herein and in the claims "degree of hydrolysis" is the ratio of the number of hydroxyl groups to the sum of the number of hydroxyl groups and the number of unreacted hydrolyzable ester groups present in the poly(vinyl alcohol), multiplied by one hundred. The degree of 10 hydrolysis is expressed as percent.

The weight average molecular weight of the water-soluble poly(vinyl alcohol) may vary widely. In general, the weight average molecular weight should be at least as large as will permit the poly(vinyl alcohol) to form films, but not so 15 large as will render the binder insoluble in the volatile aqueous solvent. Usually the weight average molecular weight of the water-soluble poly(vinyl alcohol) is in the range of from 100,000 to 400,000. Often the weight average molecular weight is in the range of from 110,000 to 300,000. From 20 to 120,000 to 200,000 is preferred.

The ratio of the hydroxyl equivalents of the water-soluble poly(vinyl alcohol) to the carboxyl equivalents of the water-soluble poly[(meth)acrylic acid] (hereinafter "the hydroxyl:carboxyl equivalent ratio") in the coating 25 composition may vary considerably, but usually it is in the range of from 0.3:1 to 3:1. In many instances the hydroxyl:carboxyl equivalent ratio is in the range of from 0.5:1 to 2:1. From 0.7:1 to 1.5:1 is preferred.

Other thermoplastic film-forming organic polymer may 30 also be present in the binder so long as its presence does not confer water-insolubility upon the binder of the coating composition or materially affect the properties of the coating in an adverse manner. The amount of the other thermoplastic

- 7 -

polymer which may be present depends upon the nature of such polymer. In general, a greater amount of other thermoplastic organic polymer may be used if the molecular structure contains many hydroxyl or carboxyl groups, than when there are 5 few such groups. Usually the other thermoplastic polymer, when present, constitutes no more than 30 percent by weight of the binder. In most cases the other thermoplastic organic film-forming polymer is substantially absent.

The amount of poly(vinyl alcohol) and 10 poly[(meth)acrylic acid] collectively present in the binder may also vary widely. In most instances the poly(vinyl alcohol) and the poly[(meth)acrylic acid] constitute from 70 to 100 percent by weight of the binder. Frequently the poly(vinyl alcohol) and the poly[(meth)acrylic acid] 15 constitute from 85 to 100 percent by weight of the binder. From 95 to 100 percent by weight is preferred. It is especially preferred that the poly(vinyl alcohol) and the poly[(meth)acrylic acid] constitute substantially all of the binder.

20 Water-soluble crosslinking agents may optionally be present in the binder of the coating composition. These crosslinking agents are water-soluble compounds which will react with hydroxyl and/or carboxyl groups upon exposure of a coating formed from the coating composition to heat or other 25 conditions which will cause the crosslinking reaction to ensue. Examples of suitable water-soluble crosslinking agents include low molecular weight melamine-aldehyde resin, low molecular weight resorcinol-aldehyde resin, low molecular weight phenol-aldehyde resin, glyoxal, gluteraldehyde, 30 acetaldehyde, formaldehyde, boric acid, and sodium borate.

- 8 -

When present, water-soluble crosslinking agent usually constitutes less than 10 percent by weight of the binder.

Preferably when present the water-soluble crosslinking agent constitutes less than 5 percent by weight of the binder.

5 Minor amounts, usually less than 5 percent by weight, of other materials introduced for particular purposes may optionally be present in the binder. Examples of such optional materials include surfactants, antioxidants, ultraviolet light absorbers, dyes, and the like. The balance
10 of the binder is substantially thermoplastic organic polymer.

All constituents of the binder of the coating composition are water-soluble. Although all constituents of the binder of the coating of the printing medium are usually water-soluble, this is not always so since one or more of such
15 constituents may be crosslinked even to the point of water insolubility.

Many different types of particulate hydrophilic amorphous silicas are known and have been used in a wide variety of applications. The most prevalent of the particulate hydrophilic amorphous silicas are the particulate hydrophilic amorphous precipitated silicas, the particulate hydrophilic amorphous silica gels, the colloidal particulate hydrophilic amorphous silicas, and the particulate hydrophilic amorphous fumed silicas. The particulate hydrophilic
25 amorphous silica may be a single particulate hydrophilic amorphous silica, or it may be a mixture of two or more particulate hydrophilic amorphous silicas of the same type and/or of different types.

It is important to distinguish amorphous
30 precipitated silica from amorphous silica gel inasmuch as these different materials have different properties.

Reference in this regard is made to R. K. Iler,
The Chemistry of Silica, John Wiley & Sons, New York (1979),

- 9 -

Library of Congress Catalog Card No. QD 181.S6144. Note especially pages 15-29, 172-176, 218-233, 364-365, 462-465, 554-564, and 578-579, the disclosures of which are incorporated herein by reference.

5 Amorphous silica gel is usually produced commercially at low pH by acidifying an aqueous solution of a soluble metal silicate, customarily sodium silicate, with acid. The acid employed is generally a strong mineral acid such as sulfuric acid or hydrochloric acid although carbon
10 dioxide is sometimes used. Inasmuch as there is essentially no difference in density between the gel phase and the surrounding liquid phase while the viscosity is low, the gel phase does not settle out, that is to say, it does not precipitate. Silica gel, then, may be described as a
15 non-precipitated, coherent, rigid, three-dimensional network of contiguous particles of colloidal amorphous silica. Following gel formation the liquid is removed by drying. The state of subdivision of amorphous silica gel ranges from large, solid masses to submicroscopic particles, and the
20 degree of hydration from almost anhydrous silica to soft gelatinous masses containing on the order of 100 parts of water per part of silica by weight, although the highly hydrated forms are only rarely used. Amorphous aerogel is a class of amorphous silica gel which is produced by (a) forming
25 amorphous silica gel by acidification in the conventional manner, (b) replacing most of the water in the gel with a liquid such as 1-propanol which wets the surface of the silica gel pores, has a very low surface tension, and evaporates at ordinary temperature, and then (c) removing the liquid under
30 pressure above the critical temperature of the alcohol so that there is no meniscus between the liquid and gas phases.

- 10 -

Amorphous precipitated silica is usually produced commercially by combining an aqueous solution of a soluble metal silicate, ordinarily alkali metal silicate such as sodium silicate, and an acid so that colloidal particles will grow in weakly alkaline solution and be coagulated by the alkali metal ions of the resulting soluble alkali metal salt. 5 Various acids may be used, including the mineral acids and/or carbon dioxide. In the absence of a coagulant, silica is not precipitated from solution at any pH. The coagulant used to 10 effect precipitation may be the soluble alkali metal salt produced during formation of the colloidal silica particles, it may be added electrolyte such as a soluble inorganic or organic salt, or it may be a combination of both. Processes for producing amorphous precipitated silicas and the 15 properties of the products are described in detail in United States Patents No. 2,657,149; 2,940,830; 4,132,806; 4,495,167, 4,681,750, and 5,094,829.

Amorphous precipitated silica, then, may be described as precipitated aggregates of ultimate particles of 20 colloidal amorphous silica which aggregates have not at any point existed as macroscopic gel during the preparation. The sizes of the aggregates and the degree of hydration may vary widely.

Amorphous precipitated silica powders differ from 25 amorphous silica gels that have been pulverized in ordinarily having a more open structure, that is, a higher specific pore volume. However, the specific surface area of amorphous precipitated silica as measured by the Brunauer, Emmett, Teller (BET) method using nitrogen as the adsorbate, is often 30 lower than that of amorphous silica gel.

Variations in the parameters and/or conditions during production result in variations in the types of amorphous precipitated silicas produced. Although they are

- 11 -

all broadly amorphous precipitated silicas, the types of amorphous precipitated silicas often differ significantly in physical properties and sometimes in chemical properties. These differences in properties are important and often result 5 in one type being especially useful for a particular purpose but of marginal utility for another purpose, whereas another type is quite useful for that other purpose but only marginally useful for the first purpose.

Colloidal amorphous silica is also known. Its 10 preparation and properties are described by R. K. Iler in The Chemistry of Silica, John Wiley & Sons, Inc., New York (1979) ISBN 0-471-02404-X, pages 312-337, and in United States Patents No. 2,601,235; 2,614,993; 2,614,994; 2,617,995; 2,631,134; 2,885,366; and 2,951,044, the disclosures of which 15 are, in their entireties, incorporated herein by reference.

Examples of commercially available colloidal amorphous silica include Ludox® HS, LS, SM, TM and CL-X colloidal amorphous silica (E. I. du Pont de Nemours & Company, Inc.) in which the counter ion is the sodium ion, and Ludox® AS colloidal 20 amorphous silica (E. I. du Pont de Nemours & Company, Inc.) in which the counter ion is the ammonium ion. Another example is Ludox® AM colloidal amorphous silica (E. I. du Pont de Nemours & Company, Inc.) in which some of the silicon atoms have been replaced by aluminum atoms and the counter ion is 25 the sodium ion.

Amorphous fumed silica, also known as amorphous pyrogenic silica, is well known. It is formed at high temperature and is recovered from the gas phase as a voluminous, extremely finely divided powder. Amorphous fumed 30 silica may be made by any of several pyrogenic processes, including (1) vaporizing silicon dioxide in an arc or plasma jet and condensing it in a stream of dry inert gas, (2) oxidizing silicon monoxide in the vapor phase with oxygen

- 12 -

and condensing the silicon dioxide, (3) oxidizing silicon compounds such as SiH₄, SiCl₄, or HSiCl₃, with oxygen in a hydrocarbon flame, (4) oxidizing silicon esters such as ethyl silicate; and (5) hydrolyzing SiCl₄, SiF₄, or silicon esters such as methyl silicate, ethyl silicate, or butyl silicate at high temperatures. Other processes are known. See generally R. K. Iler, The Chemistry of Silica, John Wiley & Sons, New York (1979), Library of Congress Catalog Card No. QD181.S6144. Note especially pages 25, 336-337, 565-568, 10 613-614, and 632-633, the disclosures of which are incorporated herein by reference.

The hydrophilic amorphous silica used in the present invention is particulate. The particulate hydrophilic amorphous silica may be in the form of aggregates of ultimate particles, agglomerates of aggregates, or a combination of both. The gross particle sizes of the particulate hydrophilic amorphous silica used in the present invention may vary widely but ordinarily at least about 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.01 to 25 micrometers (μm). Frequently at least about 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.05 to 20 μm . In many cases at least about 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.1 to 10 μm . Often at least 90 percent by weight of the amorphous silica has gross particle sizes in the range of from 0.1 to 5 μm . Preferably at least 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.1 to 2 μm . Size reduction and/or classification may be used to adjust gross particle sizes as necessary or as desired. Gross particle

- 13 -

sizes in the range of from about 0.01 to about 0.6 μm are determined by photon correlation spectroscopy using a Coulter Model N4SD analyzer and size distribution processor analysis in accordance with the accompanying operating manual; see also

5 "Coulter[®] Model N4 series analyzers. Sizing by photon correlation spectroscopy." (Coulter Electronics, Inc., Hialeah, FL, 4 pages, 1987). Gross particle sizes in the range of from about 0.6 to about 125 μm are determined by use of a Model TAII Coulter Counter[®] (Coulter Electronics, Inc.)

10 according to ASTM C 690-80 but modified by stirring the amorphous silica particles for 10 minutes in Isoton[®] II electrolyte (Curtin Matheson Scientific, Inc.) using a four-blade, 4.45 centimeter diameter propeller stirrer. It is expected that the sizes of silica agglomerates may be reduced

15 during processing of the ingredients to prepare the coating composition. Accordingly, the distribution of gross particle sizes in the coating composition may be smaller than that of the raw amorphous silica used to prepare the coating composition.

20 The BET surface area of the dried particulate hydrophilic amorphous silica used in the present invention may vary widely. In many cases the BET surface area is in the range of from 100 to 1000 square meters per gram (m^2/g). Often the BET surface area is in the range of from 100 to 500 m^2/g .

25 From 125 to 225 m^2/g is preferred. As used in the present specification and claims, the BET surface area of the dried amorphous silica is the surface area determined by the Brunauer, Emmett, Teller (BET) method according to ASTM C 1993-91 using nitrogen as the adsorbate.

30 The dibutyl phthalate ("DBP") oil absorption of the particulate hydrophilic amorphous silica used in the present invention may vary widely. In many instances the DBP oil absorption is in the range of from 100 to 300 cubic

- 14 -

centimeters per 100 grams ($\text{cm}^3/100\text{g}$). Often the DBP oil absorption is in the range of from 150 to 250 $\text{cm}^3/100\text{g}$. From 175 to 225 $\text{cm}^3/100\text{g}$ is preferred. As used in the present specification and claims, DBP oil absorption of the particles 5 is determined according to ASTM D 2414-93 using dibutyl phthalate [CAS 84-74-2] as the absorbate and a Type E Absorptometer with the procedure modified as follows: (1) a sample of amorphous silica weighing 12.5 ± 0.1 grams (g) which is not further dried is introduced to the Type E 10 Absorptometer, (2) the moisture content of another sample of the amorphous silica weighing between 10 and 11 grams is determined using an Ohaus® moisture balance (Ohaus Corporation, Florham Park, NJ) with settings at 160°C and 10 minutes, and (3) the DBP oil absorption is calculated 15 from the equation:

$$\text{OA} = 100V/S + 3.9(M - 1.7)$$

where:

20 OA is the DBP oil absorption, $\text{cm}^3/100\text{g}$,
V is the volume of dibutyl phthalate used, cm^3 ,
S is the weight of the amorphous silica sample, g, and
M is the moisture content, percent H_2O by weight.

25 The amorphous silica:binder weight ratio of the coating composition and of the coating of the coated substrate may vary widely but usually it is in the range of from 0.5:1 to 2:1. In many cases the amorphous silica:binder weight ratio is in the range of from 0.85:1 to 1.25:1. An amorphous 30 silica:binder weight ratio in the range of from 0.95:1 to 1.05:1 is preferred.

The amount of volatile aqueous solvent present in the coating compositions of the invention may vary very

- 15 -

widely. In general, at least enough volatile aqueous solvent should be present to dissolve the binder. The maximum amount is not limited by any theory, but by practical considerations such as the time and cost to remove the volatile aqueous solvent from the coating after application. In most cases the volatile aqueous solvent constitutes from 80 to 99 percent by weight of the coating composition. Often the volatile aqueous solvent constitutes from 82 to 95 percent by weight of the coating composition. From 4 to 90 percent by weight is preferred. Accordingly, the binder and the particulate hydrophilic amorphous silica collectively usually constitute from 1 to 20 percent by weight of the coating composition. Frequently the binder and the particulate hydrophilic amorphous silica collectively constitute from 5 to 18 percent by weight of the coating composition. From 10 to 16 percent by weight is preferred.

The coating compositions of the invention are usually prepared by simply admixing the various ingredients. Although the mixing is usually accomplished at room temperature, elevated temperatures are sometimes used. The maximum temperature which is usable depends upon the heat stability of the ingredients. Temperatures above about 100°C are only rarely employed.

The coating compositions of the invention are generally used to form adherent coatings on substrates. The substrate is coated with the coating composition using substantially any technique known to the art. These include spraying, curtain coating, dipping, roller application, printing, brushing, drawing, and extrusion.

Substrates which may be coated with the coating compositions of the invention may vary widely in their identities and their properties. The substrate may be transparent or it may be opaque. Organic substrates such as

- 16 -

wood, fiberboard, particle board, composition board, paper, cardboard and various polymers such as polyolefins (especially polyethylene and polypropylene), polyesters (especially poly(ethylene terephthalate)), polyamides, cured phenolic resins, cured aminoplasts, polystyrene, and poly(meth)acrylates. Inorganic substrates are exemplified by glass, quartz, and ceramic materials. Many metallic substrates may be coated. Exemplary metallic substrates are iron, steel, stainless steel, copper, brass, bronze, aluminum, magnesium, titanium, nickel, chromium, zinc, and alloys.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The invention is further described in conjunction with the following examples which are to be considered illustrative rather than limiting, and in which all parts are parts by weight and all percentages are percentages by weight unless otherwise specified.

EXAMPLE 1

A poly(vinyl alcohol) (PVOH) solution was formed by dissolving 100 grams polyvinyl alcohol (Airvol® 540; Air Products Inc., Allentown, PA) having a degree of hydrolysis of 87-89% and a weight average molecular weight of 124,000 - 186,000 in 900 grams of deionized water. The mixture was stirred at elevated temperature (80 - 90°C) until all polyvinyl alcohol was dissolved giving a composition containing approximately 10 percent solids by weight.

To 25 grams of the above PVOH solution was added 16.3 grams of a 25 percent by weight aqueous solution of poly(acrylic acid) (PAA) having a weight average molecular weight of 240,000, and 40 grams of deionized water. This

- 17 -

mixture was stirred to form a homogeneous solution. To the PVOH/PAA solution, 6.6 grams of a finely divided particulate hydrophilic amorphous precipitated silica (Hi-Sil® T-600; PPG Industries, Inc., Pittsburgh, PA) was added while stirring 5 to form a coating composition.

The coating composition was applied to a polypropylene film having a thickness of 25.4 micrometers using a Meyer Rod #24 and allowed to dry under an infrared heating lamp. The dry coating was about 1 to 2 micrometers 10 thick and exhibited good adhesion to the polypropylene film as demonstrated by a lack of cracking or delamination during a 180 degree flex/bend test.

The coated polypropylene film was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and 15 a Hewlett-Packard 850C ink jet printer. The printed film showed good image quality and high color fidelity.

EXAMPLE 2

A coating composition was prepared as described in 20 Example 1. The coating composition was applied to a poly(ethylene terephthalate) (PET) substrate using a Meyer Rod #24 and allowed to dry under an infrared heating lamp. The dry coating was approximately 1 to 2 micrometers thick and was translucent.

25 The coated PET substrate was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed substrate showed good image quality and high color fidelity.

30

EXAMPLE 3

In a beaker, 16.5 grams of a 40% colloidal particulate hydrophilic amorphous silica solution (Ludox® HS-40; E. I. du Pont de Nemours & Co., Wilmington, DE) was added

- 18 -

to 16.3 grams of a 25 percent by weight aqueous solution of poly(acrylic acid) having a weight average molecular weight of 240,000. Addition of the colloidal silica solution to the PAA solution while stirring resulted in the solution turning milky
5 white; however, no precipitate was observed. Next, 25 grams of the PVOH solution described in Example 1 was added to the PAA/colloidal silica mixture followed by an additional 25 grams of deionized water to form a coating composition.

The coating composition was applied to a
10 polypropylene film having a thickness of 25.4 micrometers using a Meyer Rod #24 and allowed to dry under an infrared heating lamp. The dry coating was about 1 to 2 micrometers thick and exhibited good adhesion to the polypropylene film as demonstrated by a lack of cracking or delamination during a
15 180 degree bend/flex test.

The coated polypropylene film was then printed on the coated side by a Hewlett-Packard 850C ink jet printer. The printed film showed good image quality and high color fidelity.

EXAMPLE 4 (Comparative)

To 50.3 grams of the PVOH solution described in Example 1 was added 32.7 grams of a 25 percent aqueous solution of poly(acrylic acid) having a weight average molecular weight of 240,000 and 25 grams of deionized water.
25 This mixture was stirred to form a homogeneous coating composition which contained no amorphous silica.

The coating composition was applied to a poly(ethylene terephthalate) substrate with a Meyer Rod #150 and allowed to dry under an infrared heating lamp. The dry coating was approximately 20 micrometers thick, clear, and sticky to the touch.
30

- 19 -

The coated PET substrate was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed PET substrate exhibited unacceptable image quality with 5 substantial cracking within the black pigmented regions.

EXAMPLE 5 (Comparative)

To 25 grams of the PVOH solution described in Example 1 was added 3 grams of a 40 percent by weight nonionic 10 maleated polypropylene (PP) emulsion (Poly Emulsion 43N40; ChemCor Inc., Chester, NY) and 35 grams of deionized water. This mixture was stirred to form a homogeneous solution. To the PVOH/PP solution, 3.75 grams of a finely divided particulate hydrophilic amorphous precipitated silica (Hi-Sil® 15 T-600; PPG Industries Inc., Pittsburgh, PA) was added while stirring to form a coating composition.

The coating composition was applied to a polypropylene film having a thickness of 25.4 micrometers using a Meyer Rod #24 and allowed to dry under an infrared 20 heating lamp. The dry coating was about 1 to 2 micrometers thick and exhibited good adhesion to the polypropylene film.

The coated polypropylene film was then printed on the coated side by a Hewlett-Packard 1600C ink jet printer and a Hewlett-Packard 850C ink jet printer. The printed film 25 showed poor image quality with a high amount of bleed.

Although the present invention has been described with reference to specific details of certain embodiments thereof, it is not intended that such details should be regarded as limitations upon the scope of the invention except 30 insofar as they are included in the accompanying claims.

- 20 -

CLAIMS:

1. A coating composition comprising:
 - (a) volatile aqueous solvent;
 - (b) binder dissolved in the volatile aqueous solvent, the binder comprising water-soluble poly[(meth)acrylic] acid and water-soluble poly(vinyl alcohol); and
 - (c) particulate hydrophilic amorphous silica wherein at least 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.01 to 25 μm .

15 2. The coating composition of claim 1 wherein water constitutes at least 95 percent by weight of the volatile aqueous solvent.

3. The coating composition of claim 1 wherein

20 water constitutes substantially all of the volatile aqueous solvent.

4. The coating composition of claim 1 wherein the water-soluble poly[(meth)acrylic] acid is water-soluble poly(acrylic acid).

5. The coating composition of claim 1 wherein the water-soluble poly[(meth)acrylic] acid is water-soluble poly(methacrylic acid).

30

6. The coating composition of claim 1 wherein the water-soluble poly[(meth)acrylic] acid is a water-soluble copolymer of acrylic acid and methacrylic acid.

- 21 -

7. The coating composition of claim 1 wherein the weight average molecular weight of the water-soluble poly[(meth)acrylic] acid is in the range of from 100,000 to 5 1,000,000.

8. The coating composition of claim 1 wherein the degree of hydrolysis of the water-soluble poly(vinyl alcohol) is at least .5 percent.

10

9. The coating composition of claim 1 wherein the weight average molecular weight of the water-soluble poly(vinyl alcohol) is in the range of from 100,000 to 400,000.

15

10. The coating composition of claim 1 wherein the hydroxyl:carboxyl equivalent ratio is in the range of from 0.3:1 to 3:1.

20

11. The coating composition of claim 1 wherein the water-soluble poly[(meth)acrylic] acid and the water-soluble poly(vinyl alcohol) constitute from 70 to 100 percent by weight of the binder.

25

12. The coating composition of claim 1 wherein the water-soluble poly[(meth)acrylic] acid and the water-soluble poly(vinyl alcohol) constitute substantially all of the binder.

30

13. The coating composition of claim 1 wherein the binder comprises water-soluble crosslinking agent and wherein the water-soluble crosslinking agent constitutes less than 10 percent by weight of the binder.

14. The coating composition of claim 1 wherein the particulate hydrophilic amorphous silica is particulate hydrophilic amorphous precipitated silica.

5

15. The coating composition of claim 1 wherein:

- (a) the BET surface area of the particulate hydrophilic amorphous silica is in the range of from 100 to 1000 m²/g, and
- 10 (b) the DBP oil absorption of the particulate hydrophilic amorphous silica is in the range of from 100 to 300 cm³/100g.

16. The coating composition of claim 1 wherein the
15 amorphous silica:binder ratio is in the range of from 0.5:1 to
2:1.

17. The coating composition of claim 1 wherein:

- (a) the volatile aqueous solvent constitutes from
20 80 to 99 percent by weight of the coating composition, and
- (b) the binder and the particulate hydrophilic amorphous silica collectively constitute from 1 to 20 percent by weight of the coating composition.

25

- 23 -

18. A printing medium comprising:

- (a) a substrate having at least one surface; and
- (b) a coating on the surface wherein the coating comprises:

5

- (1) binder comprising poly[(meth)acrylic] acid and poly(vinyl alcohol); and
- (2) particulate hydrophilic amorphous silica dispersed in the binder, wherein at least 90 percent by weight of the particulate hydrophilic amorphous silica has gross particle sizes in the range of from 0.01 to 25 μm .

10

19. The printing medium of claim 18 wherein the
15 poly[(meth)acrylic] acid is poly(acrylic acid).

20. The printing medium of claim 18 wherein the
poly[(meth)acrylic] acid is poly(methacrylic acid).

21. The printing medium of claim 18 wherein the
poly[(meth)acrylic] acid is a copolymer of acrylic acid and
methacrylic acid.

22. The printing medium of claim 18 wherein the
25 weight average molecular weight of the poly[(meth)acrylic]
acid is in the range of from 100,000 to 1,000,000.

23. The printing medium of claim 18 wherein the
degree of hydrolysis of the poly(vinyl alcohol) is at least 75
30 percent.

- 24 -

24. The printing medium of claim 18 wherein the weight average molecular weight of the poly(vinyl alcohol) is in the range of from 100,000 to 400,000.

5 25. The printing medium of claim 18 wherein the hydroxyl:carboxyl equivalent ratio is in the range of from 0.3:1 to 3:1.

10 26. The printing medium of claim 18 wherein the poly[(meth)acrylic] acid and the poly(vinyl alcohol) constitute from 70 to 100 percent by weight of the binder.

15 27. The printing medium of claim 18 wherein the poly[(meth)acrylic] acid and the poly(vinyl alcohol) constitute substantially all of the binder.

20 28. The printing medium of claim 18 wherein the binder comprises crosslinking agent and wherein the crosslinking agent constitutes less than 10 percent by weight of the binder.

25 29. The printing medium of claim 18 wherein the particulate hydrophilic amorphous silica is particulate hydrophilic amorphous precipitated silica.

30. The printing medium of claim 18 wherein:

- (a) the BET surface area of the particulate hydrophilic amorphous silica is in the range of from 100 to 1000 m²/g, and
- 30 (b) the DBP oil absorption of the particulate hydrophilic amorphous silica is in the range of from 100 to 300 cm³/100g.

- 25 -

31. The printing medium of claim 18 wherein the amorphous silica:binder ratio is in the range of from 0.5:1 to 2:1.

5 32. The printing medium of claim 18 wherein the binder and the particulate hydrophilic amorphous silica collectively constitute from 1 to 20 percent by weight of the coating.

10 33. The printing medium of claim 18 wherein the substrate is transparent.

34. The printing medium of claim 18 wherein the substrate is opaque.

15 35. A printing process which comprises applying liquid ink droplets to the printing medium of claim 18.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/09882

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B41M5/00 C09D133/02 C09D129/04

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B41M C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 892 787 A (KRUSE JURGEN M ET AL) 9 January 1990 see column 1, line 24 - column 2, line 2 see column 2, line 62 - column 4, line 29 see column 4, line 65 - column 7, line 24 ---	1-35
A	DATABASE WPI Section Ch, Week 8541 Derwent Publications Ltd., London, GB; Class A14, AN 85-253527 XP002072989 & JP 60 168 651 A (KURARAY CO LTD) see abstract	1, 18, 35
A	EP 0 233 703 A (ICI PLC) 26 August 1987 see page 2, line 24 - page 4, line 28 ---	1, 18, 35

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on, or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

10 August 1998

18/08/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Markham, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/09882

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8804 Derwent Publications Ltd., London, GB; Class A18, AN 88-026206 XP002072990 & JP 62 288 076 A (HONSHU PAPER MFG CO LTD) see abstract -----	1, 18, 35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/09882

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4892787	A 09-01-1990	NONE		
EP 0233703	A 26-08-1987	CA 1291909 A DE 3772788 A JP 2030731 C JP 7061742 B JP 62218181 A US 4857386 A		12-11-1991 17-10-1991 19-03-1996 05-07-1995 25-09-1987 15-08-1989

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)